

# Thermoelectric properties in Mn-doped Bi<sub>2</sub>Se<sub>3</sub>

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## ABSTRACT

Using n-type and p-type Mn-doped Bi<sub>2</sub>Se<sub>3</sub> single crystals, a thin-film-type thermoelectric (TE) module was fabricated and the TE characteristics were investigated. The Seebeck coefficient at room temperature was about 100  $\mu\text{V K}^{-1}$  with different sign for both materials. From the Seebeck coefficient and resistivity values, the electric power of our TE module was evaluated to be 90  $\mu\text{W}$  for a single couple at the temperature difference of 10 K. This value is compared to that ( $\sim 21 \mu\text{W}$ ) of commercialized TE device. Nevertheless, the actual power was measured to be quite small around 0.74  $\mu\text{W}$ , which is much higher than other homemade TE power level. This small power is attributed to the high electrical contact resistance between the TE material and the heat source and sink. Assuming the contact resistance level  $\sim 0.1 \Omega$  similar to that of commercialized TE devices, the electric power should be about 41  $\mu\text{W}$ , which is almost 2 times higher than that in commercialized TE devices. These results propose that the Mn-doped Bi<sub>2</sub>Se<sub>3</sub> system is another promising TE material, which can be replaced with the commercialized Bi<sub>2</sub>Te<sub>3</sub> system.

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## 1. Introduction

We are facing global energy crisis due to increased consumption of energy and limited resource of fossil fuels. Development of alternative energy is very important in recent years [1,2]. In particular, an increasing concern of environmental issues of emission has resulted in extensive research on green technology to generate electrical power [3–8]. Among those environmentally friendly technologies, thermoelectric (TE) power generation has emerged as promising technology because it can directly convert waste heat into electrical energy [1–8]. When materials have a temperature gradient  $\Delta T$ , electric current  $I$  and voltage  $V$  (i.e. electric power  $P = IV$ ) are generated. A conventional TE module is composed of two different TE elements of n- and p-type semiconductors that are connected electrically in series and thermally in parallel. These TE elements are connected with heat source and heat sink to absorb heat and exhaust heat, respectively. The schematic diagram of basic structure of TE power generator is plotted in Fig. 1a.

A<sub>2</sub>B<sub>3</sub> (A = Bi, Sb and B = Se, Te) is a family to have good TE properties at room temperature [9]. Among them, Bi<sub>2</sub>Te<sub>3</sub> is the best

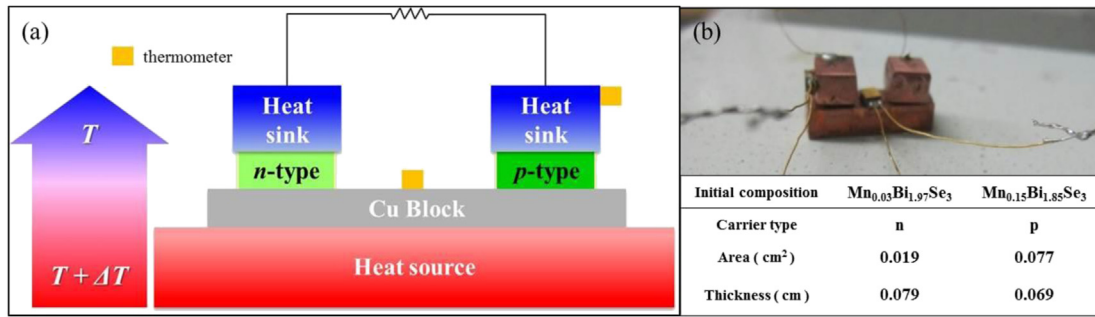
TE material used commercially in the bulk form for cooling and power generation application [2]. It is easy to manipulate n- and p-type materials by substituting other elements in Bi<sub>2</sub>Te<sub>3</sub>; for example, n-type Bi<sub>2</sub>(Te,Se)<sub>3</sub> and p-type (Bi,Sb)<sub>2</sub>Te<sub>3</sub> [4]. On the other hand, although Bi<sub>2</sub>Se<sub>3</sub> shows good TE properties [10,11], it is less used because of the difficulty in preparing p-type Bi<sub>2</sub>Se<sub>3</sub>-based materials. As-prepared Bi<sub>2</sub>Se<sub>3</sub> is normally n-type in nature [12]. In our previous study, we reported p-type Bi<sub>2</sub>Se<sub>3</sub> by Mn doping [13]. The carrier type is changed from n- to p-type for the Mn contents above 5%. Based on these observations, in the present work, we report the TE performance and the power generation of a single TE module (Fig. 1b) using both n- and p-type Mn-doped Bi<sub>2</sub>Se<sub>3</sub> materials. The samples are easily fabricated in a single crystal form, which is well cleaved in a thin-film form. These advantages such as the simply tuning of carrier types by Mn and the easy production of thin-film-type single crystals make it possible to be used for TE microdevices. First, we have determined the basic TE characteristics of Seebeck coefficient  $S$  and electrical resistivity  $\rho$  by changing Mn contents of 3% and 15%. Next, we have measured the open-circuit voltage  $V_{oc}$  and short-circuit current  $I_{sc}$ , which generates the electric power ( $P = V_{oc}I_{sc}/4$ ).

## 2. Experimental procedure

The single crystals of Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> ( $x = 0.03$  and  $0.15$ ) were prepared using melting method with stoichiometric starting

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**Fig. 1.** (a) Schematic diagram and (b) photograph of our thermoelectric module using n- and p-type Bi<sub>2</sub>Se<sub>3</sub> elements connected with heat source and sink. The inset represents the carrier type and the sample dimensions of area and thickness.

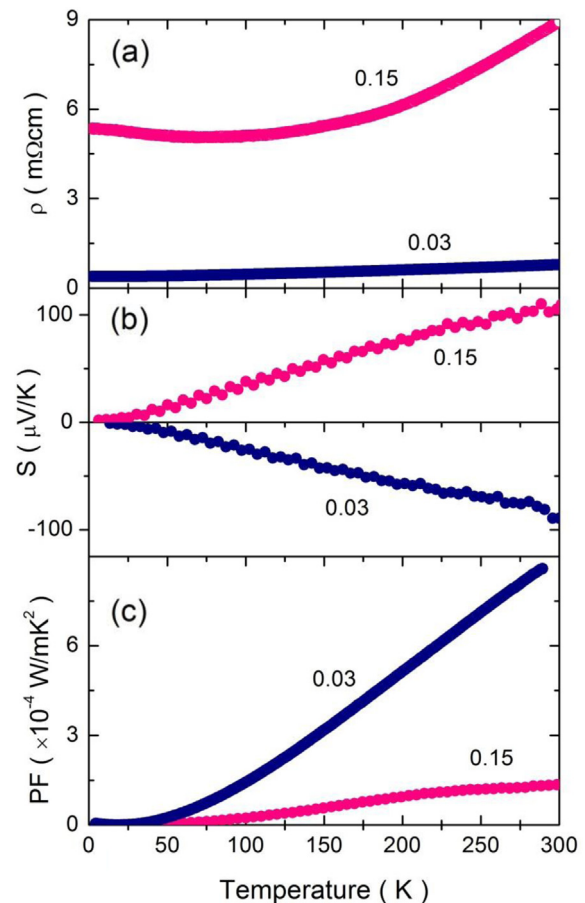
elements. In our previous report [13], we observed n-type and p-type carriers for  $x = 0.03$  and  $0.15$ , respectively, and thus we refer to the  $x = 0.03$  sample as “n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub>” and the  $x = 0.15$  sample as “p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub>”. The crystal growth methods and characterization results are described in the previous report [13]. The TE power generation performance was evaluated by measuring the electrical resistivity and Seebeck coefficient. The electrical resistivity was measured using four probe methods with the physical property measurement system. The Seebeck coefficient was measured using an alternating heating method with a laboratory made system. With these well-characterized samples, we fabricated single TE module. Fig. 1a shows the schematic diagram of basic structure of TE power generator based on the real picture of Fig. 1b. The top and bottom Cu blocks, that are of large-volume rectangular shaped, were used for heat sink heat and source. In order to improve the electrical contact, we deposited Au (99.999%) pad on the sample surfaces by using sputtering. Two different n- and p-type samples were placed on one end of heat source block, and the other ends were connected with the heat sink blocks. The samples and Cu blocks were fixed by silver paste, which could be baked up to 100 °C. For the temperature detection, the Cernox sensors were used at both top and bottom Cu blocks.

### 3. Results and discussion

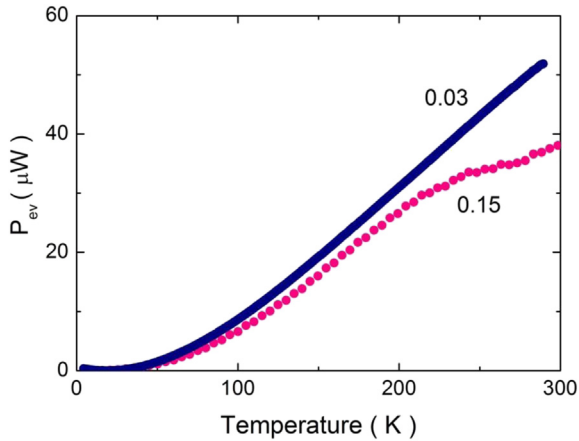
Fig. 2 shows the temperature dependence of electrical resistivity  $\rho$ , Seebeck coefficient  $S$ , and power factor (PF)  $S^2/\rho$  for both n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> and p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> samples. In Fig. 2a, the electrical resistivity of n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> monotonically decreases with decreasing temperature, which is characteristic of metallic behavior. On the other hand, the resistivity of p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> shows nonmetallic behavior at low temperatures. Here it should be mentioned that the substitution of Mn for Bi results in the enhancement of resistivity. The resistivity of p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> is much higher than that of n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub>. In Fig. 2b, the Seebeck coefficient of n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> linearly increases with temperature and it is negative in the measured temperature range, indicating the n-type carriers. This result is consistent with the previous report based on the Hall data [13]. On the other hand, the Seebeck coefficient of p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> is also linear but it is positive due to the p-type carriers. Here it should be emphasized that the absolute values of Seebeck coefficient for both samples are similar, approaching to 100  $\mu\text{V K}^{-1}$ . With these data, the power factor was evaluated as a function of temperature. As shown in Fig. 2c, the power factor for n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> is much higher, which is ascribed to the lower resistivity. The evaluated power factors at 300 K are  $9.0 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$  for n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> and  $1.5 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$  for p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub>. From these  $\rho$  and  $S$  values, we could evaluate the

electric power  $P_{\text{ev}}$  by using the relation,  $P_{\text{ev}} = (S\Delta T)^2 A / (4\rho d)$ , where  $\Delta T$  is the temperature difference,  $d$  is the sample thickness, and  $A$  is the sample area. The result is plotted in Fig. 3. In this case, we used  $\Delta T = 10 \text{ K}$  and the real sample dimensions, which were used for the thin-film-type TE power generator in the present work. The evaluated electric powers are 51.9  $\mu\text{W}$  and 38.1  $\mu\text{W}$  for n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> and p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub>, respectively. Then, a single TE module using these two materials should provide 89.9  $\mu\text{W}$  at  $\Delta T = 10 \text{ K}$  in a pair.

As described in the introduction part, we have fabricated single TE module based on the n- and p-type Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> samples. The thickness of the samples is roughly 700  $\mu\text{m}$ . Because of this thin

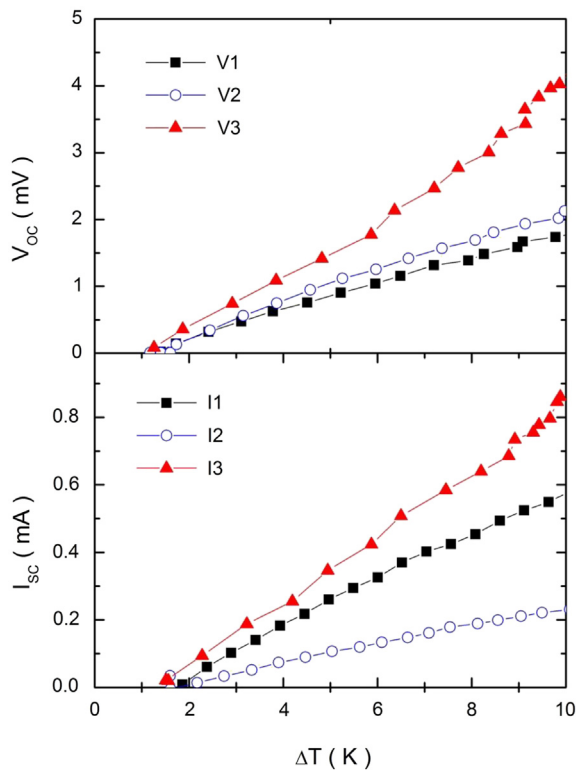


**Fig. 2.** Temperature dependence of (a) electrical resistivity  $\rho$ , (b) Seebeck coefficient  $S$ , and (c) power factor  $\text{PF} = S^2/\rho$  for both n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> and p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub>.



**Fig. 3.** Temperature dependence of evaluated electric power obtained from electrical resistivity, Seebeck coefficient, and sample dimensions of n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> and p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub>.

dimension of our samples, we would say our TE module is thin-film type. Using this single TE module staged on hot plate, the open-circuit voltage  $V_{oc}$  is monitored with changing the temperature difference  $\Delta T$ , and the short-circuit current  $I_{sc}$  is also measured in the same condition. The measured  $V_{oc}$  and  $I_{sc}$  of single TE module are plotted as a function of  $\Delta T$  in Fig. 4. The measurements were performed over 10 times with different electric contacts for different samples. The samples were taken from same Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> ingots for reproducibility. The different electric contact resistance for each TE module brings the changes in the  $V_{oc}$  and  $I_{sc}$  values, as shown in Fig. 4. Furthermore, the nonlinear relation between  $V_{oc}$



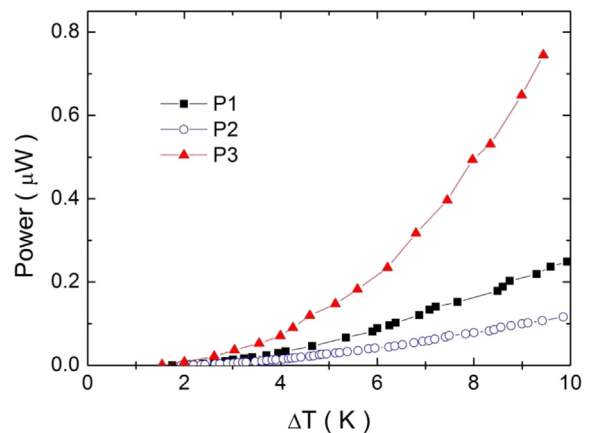
**Fig. 4.** Open-circuit voltage  $V_{oc}$  and short-circuit current  $I_{sc}$  as a function of temperature difference  $\Delta T$  for different Bi<sub>2</sub>Se<sub>3</sub>-based single thermoelectric module of 1, 2, and 3.

and  $I_{sc}$  may come from the different sample resistance. The measured open-circuit voltages  $V_1$ ,  $V_2$ , and  $V_3$  taken for different TE module are 1.77 mV, 2.07 mV, and 4.04 mV at  $\Delta T = 10$  K. The short-circuit currents  $I_1$ ,  $I_2$  and  $I_3$  are measured to be 0.58 mA, 0.22 mA, and 0.79 mA at  $\Delta T = 10$  K. Here, we would mention that we cannot make higher  $\Delta T$  because of the thin sample dimension of 700  $\mu\text{m}$ .

Based on these values, the electric power is evaluated and the results are plotted in Fig. 5. The electric power values  $P_1$ ,  $P_2$ , and  $P_3$  are 0.25  $\mu\text{W}$ , 0.12  $\mu\text{W}$ , and 0.74  $\mu\text{W}$  at  $\Delta T = 10$  K. These values are much lower than the evaluated electric power  $P_{ev}$  described above, but much higher than other homemade TE power level [14]. The origin for the different values between the evaluated and measured electric power may be the different electric contact resistance [15]. Although our TE device is composed of thin-film-type single crystals with high contact resistance, the output power in our system is almost 200 times higher than that in ref. [14], where the maximum output power at  $\Delta T = 10$  K was 0.004  $\mu\text{W}$  per single module consisting of n-type Bi<sub>2</sub>Te<sub>3</sub> and p-type Sb<sub>2</sub>Te<sub>3</sub>. However, the electric power of our TE module is not as good as that of commercialized TE devices now in use [16]. The commercial TE cooler based on Te–(Bi/Sb)–Te superlattice structures generates a power of 20.8  $\mu\text{W}$  at  $\Delta T = 10$  K. In this case, the contact resistance is about 0.1  $\Omega$ . If we assume this contact resistance level in our TE module, the electric power for  $\Delta T = 10$  K is estimated to be 41.0  $\mu\text{W}$ , which is almost 2 times higher than that in the commercial TE device [16]. Therefore, if we can achieve the similar contact resistance level to the commercial device, the Mn-doped Bi<sub>2</sub>Se<sub>3</sub> system is another promising TE material, which can be replaced with the commercialized Bi<sub>2</sub>Te<sub>3</sub> system.

#### 4. Conclusion

We have successfully made thin-film-type Mn-doped Bi<sub>2</sub>Se<sub>3</sub> single crystals, which are either n- or p-type material depending on the Mn contents. Using these two different n-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> and p-Mn<sub>x</sub>Bi<sub>2-x</sub>Se<sub>3</sub> elements, a thin-film-type TE module was fabricated and the TE characteristics were investigated. For temperature difference  $\Delta T = 10$  K, the maximum power was obtained about 0.74  $\mu\text{W}$ , which is much lower than that of commercialized TE device, but much higher than that of homemade TE module. By the assumption of contact resistance  $\sim 0.1 \Omega$  per single module, we could calculate the electric power of 41  $\mu\text{W}$ . This value is comparable or even higher than that of commercial TE generator. These results propose that the Mn-doped Bi<sub>2</sub>Se<sub>3</sub> system is a promising TE



**Fig. 5.** Electric power  $P = V_{oc}I_{sc}/4$  as a function of temperature difference  $\Delta T$  for different Bi<sub>2</sub>Se<sub>3</sub>-based single thermoelectric module of 1, 2, and 3.

material, which can be replaced with the commercialized  $\text{Bi}_2\text{Te}_3$  system.

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